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CHEMICAL EVIDENCE FOR OXIRENE INTERMEDIATES

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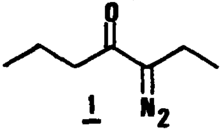
Oxirene intermediates remain a subject of considerable theoretical interest, and estimates of the energies of this unusual heterocycle continue to appear in the literature.[1] This paper presents direct chemical evidence for the appropriateness of invoking oxirenes in various reactions in which they have been proposed. The reactions of interest involve the substrates below.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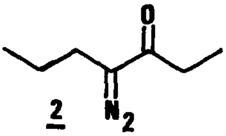
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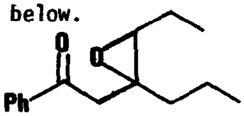
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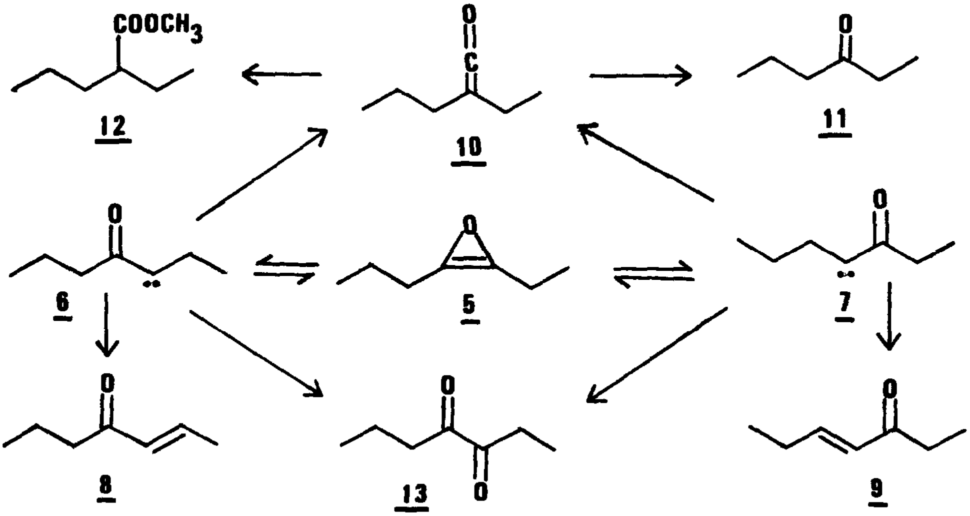
The chemical probe for oxirene intermediacy involves establishing an oxirene-oxocarbene equilibrium in which the oxirene species possesses dissimilar alkyl substituents. This technique was applied to the photodecomposition of 3-diazo-4-heptanone (1), as first reported by Matlin and Sammes[2] and later by ourselves.[3] The scheme below outlines the various transformations which account for the observed products. Thus, oxocarbene 6 is formed directly, and this species equilibrates with oxocarbene 7 by way of pseudo-symmetrical oxirene 5. The observed cis and trans enone products 8 and 9 result from hydrogen migration in the respective oxocarbenes. A minimum of 85-88% oxirene involvement in the formation of the enone products was suggested.[3] Ketene 10 is formed from alkyl migration in either oxocarbene, and it is converted to 3-hexanone (11) by adventitious oxidation or to ester 12 by reaction with methanol. The alkyl migration reduces the yield of enone products, but does not affect the chemical evidence for the oxirene-oxocarbene equilibrium.



The oxirene-oxocarbene equilibrium ($6 \rightleftharpoons 5 \rightleftharpoons 7$) may also be approached by photodecomposition of 4-diazo-3-heptanone (2),[4] which yields oxocarbene 7 directly. The results of irradiation of diazo ketone 2 at 300 nm in pentane and ether solutions are summarized in Table I.[5] The observed distribution of enone products 8 and 9 suggests 81-83% oxirene 5 involvement in this reaction.

Table I. Photodecomposition of 4-Diazo-3-heptanone (2)[a]

Solvent	Percentage Yields[b]						
	8c	8t	9c	9t	11	12	% Oxirene 5[d]
Pentane	10	9	12	15	15	—	83
Pentane (Methanol)[c]	10	9	13	15	—	28	81
Ether	11	9	13	15	16	—	82
Ether (Methanol)[c]	11	9	12	16	—	30	83

[a] Irradiations were performed in a Rayonet RPR-100 photochemical reactor equipped with RPR-3000 A lamps. The diazo ketone solutions (ca. 0.03 M) were contained in Pyrex vessels and were degassed by bubbling through nitrogen.

[b] Yields were obtained from calibrated GC measurements.

[c] Methanol was added after the irradiation was completed.

[d] $\% \text{ Oxirene} = 2\left[\frac{8c + 8t}{8c + 8t + 9c + 9t}\right] \times 100$

The final approach to the oxirene-oxocarbene equilibrium ($6 \rightleftharpoons 5 \rightleftharpoons 7$) involves direct formation of oxirene 5. Several workers have suggested oxirenes as the first-formed intermediates in peroxyacid oxidations of acetylenes.[6] Accordingly, oxidation of 3-heptyne (3) would give oxirene 5, and this species would be expected to partition itself equally between oxocarbenes 6 and 7, ultimately to yield equal amounts of 4-enones 8 and 3-enones 9. The results of m-chloroperoxybenzoic acid oxidation of 3-heptyne in methylene chloride, benzene, and ether solutions are summarized in Table II.[5] The observed equal distribution of enone products provides compelling evidence for the intermediacy of oxirene 5 in this reaction. The minor products, 3-hexanone (11) and 3,4-heptanedione (13), arise from peroxyacid oxidation of ketene 10 and oxocarbenes 8 and 9, respectively.

Table II. m-Chloroperoxybenzoic Acid Oxidation of 3-Heptyne (3)[a]

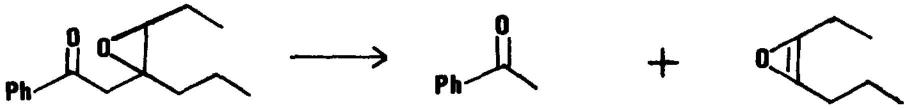
Solvent	Percentage Yields[b]						
	8c	8t	9c	9t	11	13	Enone Ratio[c]
Methylene Chloride	13	19	15	18	15	1	0.97
Benzene	8	15	8	16	18	6	0.96
Ether	11	15	11	14	18	3	1.04

[a] Approximately 0.40 M solutions of 3-heptyne were reacted with 0.25 equivalents of m-chloroperoxybenzoic acid to avoid further oxidation products. Reactions were carried out at room temperature under a nitrogen atmosphere. Reaction in methylene chloride required 6 hr, in benzene 9 hr, and in ether 163 hr.

[b] Yields were obtained from calibrated GC measurements, and based on reacted 3-heptyne.

[c] $\text{Enone Ratio} = \left[\frac{8c + 8t}{9c + 9t}\right]$

Another reaction in which oxirenes have been proposed as intermediates involves photochemical Norrish Type II cleavage of β,γ-epoxy ketones.[7] As outlined below, Type II cleavage of (E)-3,4-epoxy-1-phenyl-3-propyl-1-hexanone (4)[8] may be expected to yield oxirene 5 directly, together with acetophenone (14). As in the case of peroxyacid oxidation of 3-heptyne, because the oxirene species would be the first-formed intermediate, this approach to the oxirene-oxocarbene equilibrium (6⇆5⇄7) would ultimately yield equal amounts of enone products 8 and 9. Thus, when 0.002 M pentane or benzene solutions of epoxy ketone 4 were irradiated at 300 nm, the following products were found: 23% acetophenone, 9% trans-4-enone 8t, and 6% cis-4-enone 8c. Considerable polymerization attended the formation of these products, and no evidence was found for any additional products formed in greater than 1% yield.



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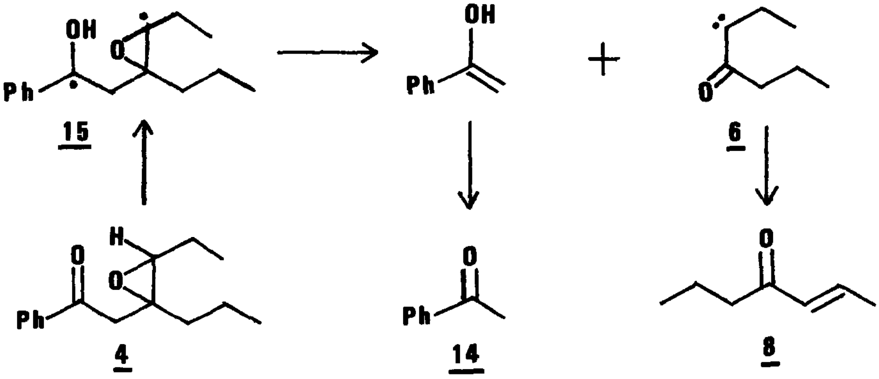
From the results obtained, it may be concluded that the desired cleavage reaction did occur, but the intermediacy of oxirene 5 in this reaction must be ruled out, because none of the isomeric 3-enones 9 could be detected. A possible pathway to account for the observed products of this photodecomposition is shown below. According to this scheme, the expected γ-hydrogen abstraction occurs to yield diradical 15, a typical Type II intermediate. This diradical species then suffers cleavage to yield the enol form of acetophenone, together with oxocarbene 6, which is a precursor of cis and trans 4-enones 8.



The failure to find evidence for an oxirene intermediate in the photodecomposition of epoxy ketone 4 may be attributed to the nature of the excited state obtained under the present conditions. As in the previously reported example of β,γ-epoxy ketone photodecomposition,[7] the transformation apparently involves a triplet excited state, since the reaction is easily quenched by 2,3-dimethyl-1,3-butadiene. Theoretical calculations[1c] predict that the singlet state of oxirene is preferred. Therefore, the energetics associated with the decomposition of epoxy ketone 4 would appear inappropriate for an oxirene intermediate. On the other hand, the photodecompositions of α-diazo ketones 1 and 2 cannot be quenched, and these reactions presumably involve singlet excited excited states from which oxirene intermediates may be obtained. Also, the ground state peroxyacid oxidation of acetylenes may yield only singlet state intermediates.

Various approaches to the oxirene-oxocarbene equilibrium ($\underline{6} \rightleftharpoons \underline{5} \rightleftharpoons \underline{7}$) have been examined. Definitive chemical evidence has been presented to support earlier suggestions of oxirenes as the intermediates in the photodecomposition of α-diazo ketones and in the peroxyacid oxidations of acetylenes. In fact, these results establish that a true equilibrium relationship exists between oxirene 5 and oxocarbenes 6 and 7. No evidence was found, however, for the proposal of an oxirene intermediate in the photodecomposition of β,γ-epoxy ketones.

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References and Notes

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2. S. A. Matlin and P. G. Sammes, *J. Chem. Soc., Perkin I*, 2623 (1972); S. A. Matlin and P. G. Sammes, *J. Chem. Soc., Chem. Commun.*, 11 (1972).
3. R. A. Cormier, K. M. Freeman, and D. M. Schnur, *Tetrahedron Lett.*, 2231 (1977).
4. 4-Diazo-3-heptanone was prepared by reaction of diazobutane with propionyl chloride in triethylamine. Expected spectroscopic and analytical properties were obtained.
5. All reaction products were independently synthesized and possessed satisfactory spectroscopic and analytical properties.
6. K. M. Ibne-Rasa, R. H. Pater, J. Ciabattoni, and J. O. Edwards, *J. Amer. Chem. Soc.*, **95**, 7894 (1973), and references cited therein.
7. A. Padwa, D. Crumrine, R. Hartman, and R. Layton, *J. Amer. Chem. Soc.*, **89**, 4435 (1967).
8. Epoxy ketone 4 was prepared by condensation of acetophenone and 4-heptanone, followed by base-catalyzed deconjugation, preparative GC separation, and peroxyacid epoxidation. Satisfactory spectroscopic and analytical properties were obtained.

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